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Study of intermolecular interactions in binary liquid mixture by ultrasonic velocity measurements

PL RM Palaniappan, A Pichaimuthu and AN Kannappan

Department of Physics, Annamalai University, Annamalai Nagar-608 002, Tamil Nadu, India

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Abstract The ultrasonic velocity in binary liquid mixtures with *m*-cresol as the common component has been measured using ultrasonic interferometric technique An attempt has been made to evaluate the sound velocity theoretically based on Nomoto's and Van Dael and Vangeel's ideal mixture relations. The percentage deviation of ultrasonic velocity, Rao's constant, molar volume and degree of molecular interaction term α are also calculated with a view to study the nature and extent of molecular interaction in the mixtures

Keywords Excess acoustical parameters, molecular interaction

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The study of intermolecular interaction attracted the attention of quite a number of investigators who used mainly infrared, NMR chemical shifts, dipole moment studies and ultraviolet methods. Ultrasonic parameters are also intensively used to study molecular interaction in pure liquids [1,2], binary and ternary liquid mixtures [3-6] and ionic interactions in single and mixed salt solutions [7,8]. Attempts have been made by a number of investigators [5,9] to correlate the non-linear variation of ultrasonic velocity and compressibility with concentration to the structural changes occurring in a liquid mixture. Jain *et al* [10] have shown that ultrasonic measurements can be used to relate even weak intermolecular interactions with acoustical parameters.

The present paper is aimed to investigate the molecular interaction in liquid mixtures of *m*-cresol with N. N. dimethylaniline, cyclohexane and aniline with special reference to the behaviour of adiabatic compressibility, molar volume, available volume and free length. The experimental findings of ultrasonic velocity with Nomoto's [11] and Ideal mixing [12] relations are also correlated.

Ultrasonic velocities of the liquid mixtures have been experimentally measured at 2 MHz using an interferometer with an accuracy of ± 0.1%. The temperature was maintained at 30°C ±

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0.1°C by an electronically controlled thermostat. The adiabatic compressibility β_a, free length L_f, molar volume V, available volume V_a and the excess parameters are calculated using the standard relations [6]. The degree of molecular interaction α is given by

$$\alpha = \frac{U_{\exp}^2}{U_{im}^2} - 1,$$

where U_{im} is calculated using the relation suggested by Van Dael and Vangeel [12].

Table 1 presents the ultrasonic velocity, adiabatic compressibility, intermolecular free length, molar volume, available volume and their excess parameters calculated for the systems Table 2 gives a summary of results on the percentage deviation of the ultrasonic velocity evaluated on the basis of Nomoto's relation, Ideal mixing relation, percentage deviation of Rao's constant, molar volume and the molecular interaction term α for the mixtures under investigation.

From the Table 2, we observe that the molecular interaction term α exhibits both positive and negative values for the system *m*-cresol with N-N dimethylaniline and aniline whereas for *m*-cresol with cyclohexane α is negative for all concentrations. We also infer that the larger value of α for cyclohexane in *m*-cresol indicates larger deviation from ideality which may be due to the existence of strong tendency for the formation of association in the mixture through hydrogen bonding as reported by Kaulgud and Patil [13]. For the system *m*-cresol with N. N dimethylaniline β_a^E changes from positive to an increasingly negative values which may be interpreted in terms of close approach of unlike molecules at higher concentration, indicating greater association. This behaviour is consistent with the findings of Adgaonkar *et al* [14].

For the system *m*-cresol with aniline L_f^E is negative for all values of concentration, whereas for the system *m*-cresol with N. N. dimethylaniline, both positive and negative values are observed. For the system *m*-cresol with cyclohexane, L_f^E is positive for all cencentrations According to Ramamurthy and Sastry [15], negative value of excess intermolecular free length L_f^E indicates that sound waves cover longer distance due to decrease in intermolecular length ascribing the dominant nature of hydrogen bond interaction between unlike molecules.

For all systems, the available volume is found to be positive for all concentrations. Fort and Moore [16] established that the positive contributions for excess value should be attributed to dispersion forces and negative excess values should be due to charge transfer, dipole-induced dipole, dipole-dipole interactions. Both positive and negative excess values observed in the present work for the systems *m*-cresol with N. N. dimethylaniline and aniline, confirms the existence of molecular interactions.

The values of ultrasonic velocities computed by Nomoto's relation and Ideal mixing relation together with the experimental values *versus* molefractions are plotted in Figure 1. From the figure, we infer that *m*-cresol + cyclohexane system shows largest deviation between theoretical and experimental values. This may be due to the formation of association in the

Table 1. Values of ultrasonic velocity, adiabatic compressibility, free length, molar volume, available volume and their excess parameters at 300°k for m-cresol with N. N Dimethylaniline, cyclohexane and aniline

Mole fraction	Density Kgm^{-3}	Velocity m/s	Adiabatic compressibility $\beta_a \times 10^{11} m^2/N$	Excess compressibility $\beta_a^E \times 10^{11}$ m^2/N	Free length L_f pm10^{-12}	Excess free length $L_f^E \times 10^{-12}$	Molar volume $V \times 10^6$ m^3/mole	Excess molar volume $V^E \times 10^6$ m^3/mole	Available volume $V_a \times 10^6$ m^3/mole	Excess available volume $V_a^E \times 10^6$ m^3/mole
0.1371	0.9649	1471	47.8928	0 0740	42 9068	0 0394	123 5664	−0.1406	9 9625	−0.0137
0.2714	0.9761	1473	47.2147	0 0231	42 602	0 0211	120 3780	−0 3925	9 5550	−0.0020
0.3812	0.9837	1475	46 7219	0 0432	42.3791	0 0322	118 0089	−0.3602	9.2194	−0 0227
0.4995	0 9914	1477	46.2357	0 1099	42.158	0.0636	115.5610	−0 2192	8 8837	−0.0104
0.6052	0 9996	1479	45 7326	0 1005	41 923	0 0591	113 2525	−0.2163	8.5647	−0.0114
0.6576	1.0063	1481	45 3056	(−)0.0816	41.7318	(−)0 0253	111.8285	−0 4939	8 3172	−0 0240
0.7532	1 0113	1483	44.9579	(−)0 0167	41 5714	(−)0 0179	110 0548	−0.1789	8.0477	−0.0730
0.8413	1.0190	1485	44 4978	(−)0.0317	41.3581	(−)0 0074	108 1098	−0 1969	7.7703	−0 0730
0 9195	1.0258	1487	44 0845	(−)0.0767	41 1656	(−)0.0331	106 4130	−0.1832	7.5154	−0 0807
0 1094	0.7996	1248	80.2946	2.1604	55 5564	0.9592	106 2795	0.6025	23 3814	0.8218
0.2134	0 8279	1256	76.5601	2.4395	54 2491	1.2377	105.9067	0.3948	22.7699	1.3097
0 3151	0.8646	1271	71 5955	1 3947	52 4607	0 9979	104 4742	0 9504	21.4824	1 0571
0.4058	0.8741	1258	69.2809	2.5799	51.6057	1 5257	106.0343	0.6876	20.8754	1.5247
0 5136	0.9039	1315	63 9757	1 4327	49 5905	1 5340	105 6390	0 3859	18 8171	0 9485
0 6090	0.9300	1338	60.0594	1 1945	48.0487	1.0648	105.3370	0 1658	17 2490	0.9010
0.7085	0.9557	1368	55 9063	0.8784	46 3577	0 8898	105.2050	0 1189	15.2547	0.7335
0.8029	0.9804	1396	52 3343	0.9470	44 8523	0.8228	105 0580	0 0533	13.3949	0 8683
0.8999	1.0062	1439	47 9905	0 3426	42 9506	0 3984	104.8690	0.0527	10.5524	0.3853
0.2078	1.0232	1598	38.2700	0 3891	38 3549	−0 1732	93.959	−0 1506	0 1174	0 4928
0.2943	1.0242	1580	39.1084	0 1104	38 7727	−0 0281	95 143	−0.2259	1 1892	1.2597
0.3849	1.0251	1570	39.5377	0 2681	38 9849	−0.1018	96 310	−0.1969	1.8058	1.9984
0.4745	1.0272	1550	40.5211	0 1354	39 4668	−0 0975	97 526	−0.1939	3 0477	2.7651
0.5864	1 0280	1529	41 6077	0 4971	39 9924	−0 2699	99.094	−0 1419	4 3973	3.7291
0.6735	1.0283	1518	42 1986	0.5239	40 2754	−0 2781	100 342	−0.0734	5 1425	4 4797
0.7876	1 0310	1498	43 2203	0 8071	40 7601	−0.4029	101 755	−0.2052	6.4868	5 4754
0 8868	1.0312	1490	43 6788	0 6228	40 9757	−0 3054	103 195	−0.1089	7.0947	6.3437

The number of significant figures is retained for internal consistency in calculations

Table 2. The percentage deviation of ultrasonic velocity from Nomoto's relation along with percentage deviation of Ideal mixing relation, Rao's constant, molar volume and molecular interaction at 300°K.

System	Mole fraction X_A	Ultrasonic velocity $\frac{\Delta U_N}{U}$ %	Ultrasonic Velocity $\frac{\Delta U_{im}}{U}$ %	Rao's constant $\frac{\Delta R}{R}$ %	Molar volume $\frac{\Delta V}{V}$ %	Molecular interaction $\alpha = \frac{U^2_{exp}}{U^2_{im}} - 1$
	0.1371	−0.0736	−0 0396	- 0 1299	−0 1138	−0 0008
	0.2713	−0 0832	-0.0266	−0 3539	−0 3261	−0.0005
	0 3811	−0 0718	−0 0049	−0.3293	- 0.3052	- 0 0001
m-cresol	0 4995	−0 0761	-0 0059	−0.2151	−0 1897	−0 0001
+	0.6052	−0 0708	−0 0046	−0 2146	- 0.1909	−0 0001
N N Dimethylaniline	0 6576	−0 0021	−0 0598	−0.4424	−0 4417	- 0.0012
	0.7531	0 0082	0 0587	−0 1599	−0.1626	0.0011
	0 8413	0.0237	0.0595	- 0 1742	−0.1822	0.0012
	0.9195	0.0490	0 0684	−0 1558	−0.1721	0 0013
	0.1094	−4 1597	- 0 0083	−0 3380	+0 5669	−0 0165
	0 2134	−5 1662	−1 4788	−1 3141	+0.3728	- 0.0289
	0 3151	-5.5565	−1 4956	−2 7452	−0 9097	−0 0292
m-cresol	0 4058	−5.8637	- 1 6421	- 1 2566	+0 6485	−0 0320
+	0 5136	−5 1604	−1 0170	−1 3198	+0 3653	−0 0200
cyclohexane	0.6090	−4 8587	−0 9936	−1 4340	+0.1574	−0 0195
	0 7085	−4 1135	−0.7972	−1.2382 •	+0 1130	−0.0157
	0 8029	−3 4870	+0.9404	−1 0977	+0.0507	−0 0185
	0.9999	−1 8674	−0 4139	−0.6692	−0 0502	−0 0082
	0.0959	+0 6758	0 6313	+0 2602	+0 0345	+0 0127
	0 2078	+0.4828	0 3992	+0.0011	−0 1602	+0 0080
	0 2942	+0 1415	0 0371	−0 0966	−0.1438	+0 0007
m-cresol	0.3849	+0 3167	0.1995	−0 0985	−0 2044	+0 0040
+	0.4745	−0 1822	0.3049	- 0 2596	−0.1988	−0 0060
Aniline	0 5864	- 0.5933	−0 7111	- 0 3409	−0 1432	−0 0140
	0.6735	−0 5906	−0 6996	- 0.2698	−0.0732	−0 0138
	0.7876	−0.9935	−1.0732	−0.5325	−0.2016	−0 0211
	0.8869	−0.7415	−0 7884	−0 3523	−0 1055	−0 0155

The number of significant figures is retained for internal consistency in calculations.

mixture through hydrogen bonding as indicated by Kaulgud and Patil [13]. For the system *m*-cresol + cyclohexane, the ultrasonic velocity values calculated using Nomoto's relation deviates from the experimental values by 5.86% whereas those calculated from Ideal mixing relation, deviate from 1.64% which indicates that the ideal mixing relation is best suited than the Nomoto's relation. Similar trends are observed for the other systems also.

It may be concluded that

(i) The non-linear variation of available volume and other excess parameters indicates association between the components.

(ii) Ideal mixing relation is best suited with the experimental results than the Nomoto's relations.

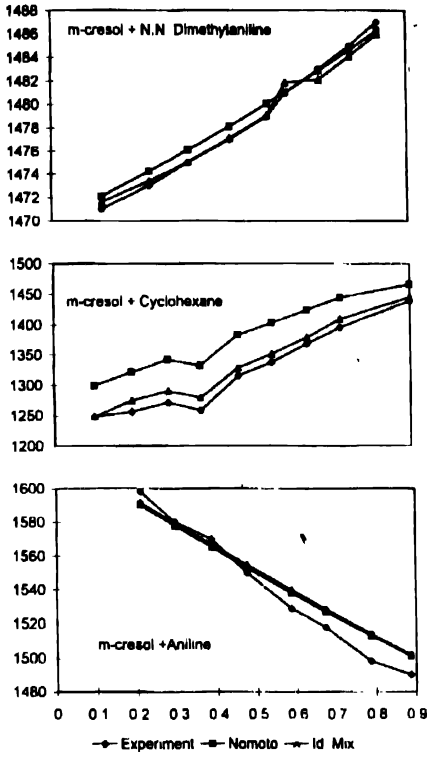

Figure 1. Variation of ultrasonic velocity against molar concentration

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